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Some Colored Amino Derivatives
of Methyl Oxomalonate

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SOME COLORED AMINO DERIVATIVES
OF METHYL OXOMALONATE

BY

ELIAS MANDEL

THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

IN THE

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1912.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Elias Mandel

ENTITLED Some Colored Amino Derivatives of Oxomalonates

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

Richard S. Carter

Instructor in Charge

APPROVED: *John H. ...*

John H. ... HEAD OF DEPARTMENT OF *Chemistry*

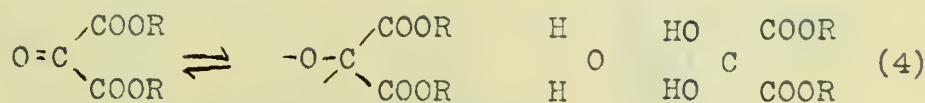


Some Colored Amino Derivatives of Oxomalonates.

Because of the extreme reactivity of the alkyl oxomalonates, it was not until comparatively a short time ago that they were obtained pure. Curtiss prepared both the ethyl¹ and methyl² oxomalonates by the action of nitrous anhydride on the corresponding malonic ester, and then distilling the dihydroxymalonate thus obtained under reduced pressure. However, he³ found that only by distillation with the strongest dehydrating agent, phosphorous pentoxide, could a perfectly pure, water-free product be obtained.

In this laboratory Curtiss and his colleagues have spent some years in the study and investigation of the unstable intermediate addition products of acids, alcohols, amines, and hydrazines upon the reactive carbonyl group of ketone esters. These addition compounds represent hypothetically the first reaction product in all such cases.

The alkyl oxomalonates combine very readily with water, alcohols, amines, and many other compounds possessing a dissociable hydrogen, as shown in the following formulae:

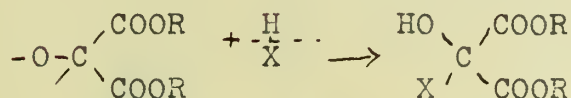
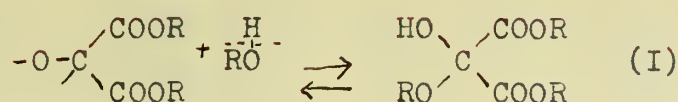


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1. Am. Chem. Jour. 35, 478.
 2. Curtiss and Tarnowski, Jour. Am. Chem. Soc. 30, 1267.
 3. Curtiss and Spencer, Jour. Am. Chem. Soc. 31, 1054.
 4. Curtiss, Am. Chem. Jour. 35, 485.

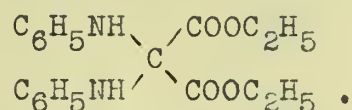


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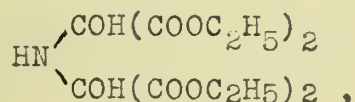
Curtiss², in the action of two molecules of aniline on a molecule of ethyl oxomalonate, obtained a substance which he found to be ethyl dianilinomalonate,



When the methyl oxomalonate was used in place of the ethyl ester, only one molecule of aniline added on, and a tartronate³ was formed. The reactivity of the ethyl keto ester is greater than that of the methyl. Curtiss⁴ previously prepared ethyl dianilinomalonate by the action of aniline on ethyl dibrommalonate, $\text{Br}_2\text{C}(\text{COOC}_2\text{H}_5)_2$. Conrad and Reinbach⁵, using the acid in place of the ester, obtained the dianilinomalonic acid. Curtiss⁶ likewise prepared ethyl dianilinomalonate by the oxidation of ethyl anilino-

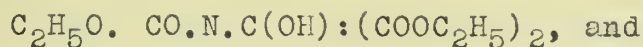
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 1. Curtiss, and Spencer, Jour. Am. Chem. Soc. 31, 1053.
 2. Am. Chem. Jour. 35, 354.
 3. Curtiss and Spencer, Jour. Am. Chem. Soc. 31, 1053.
 4. Am. Chem. Jour. 19, 695.
 5. Ber. 35, 1820.
 6. Am. Chem. Jour. 19, 694; 30, 142.

malonate, $C_6H_5NH \cdot CH(COOC_2H_5)_2$, with mercuric oxide. Ethyl anilinomalonate^I was prepared by the action of aniline on ethyl brommalonate, and in a similar way, a series containing substituting groups in the benzene ring, as ethyl ortho-, meta-, and paratoluidinomalonates², was made. By the action of dry ammonia on the ketone group Curtiss³ obtained an unstable addition product,

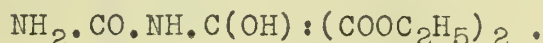


while leaving intact the usually reactive ester part of the molecule.

Curtiss and Stracham^{n 4} in their study of the action of acid amides on the ketone ester produced unstable addition products with urethan and urea, obtaining such compounds as these:



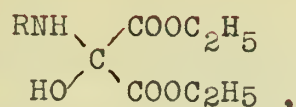
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Curtiss, Hill and Lewis⁵ studied the behavior of the three toluidines, aniline, and benzylamine on ethyl oxomalonate with the intent of obtaining the hypothetical intermediate addition product. They obtained products of the form:

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- I. Curtiss, Am. Chem. Jour. 19, 693.
2. Curtiss, Ibid. 30, 135.
3. Am. Chem. Jour. 35, 356.
4. Jour. A., Chem. Soc. 33, 396.
5. Ibid. 33, 400.



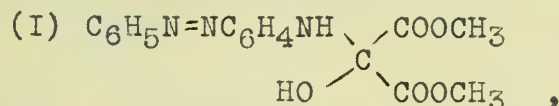
i.e., substituted aminotartrates for all but aniline.

This gave dianilinomalonate as stated above.

We have been led to try the action of aminoazobenzene on methyl oxomalonate because of the color possibility due to the presence of two chromophore groups, -N=N- (azo group) and $\text{O}=\text{C}-$. A strong reaction takes place immediately,

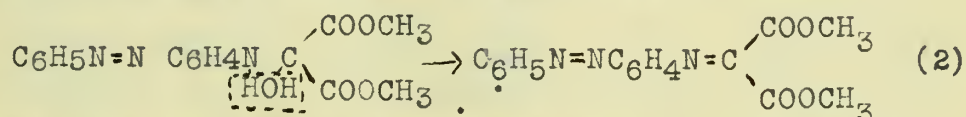


resulting in a yellow addition product,



methyl phenylazophenylaminotartrate, which is analogous to the reaction obtained by Curtiss and Spencer^I by the action of aniline on the methyl keto ester.

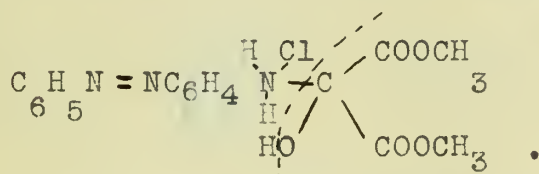
It was further endeavored to split off the elements of water from this intermediate addition product:



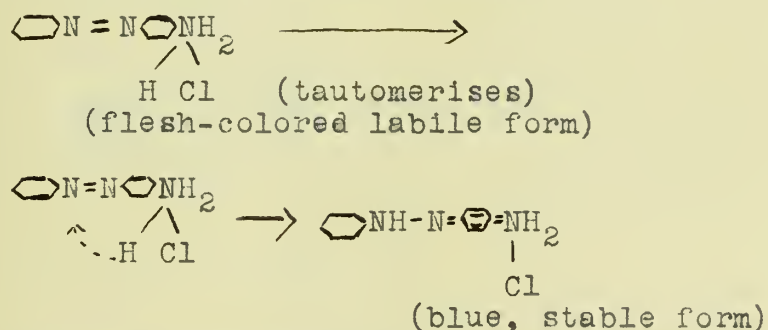
This should give two chromophore groups, -N=N-, and -N=C=, in this new compound, and a bathochromic effect would naturally be expected. Although a crimson-red product was obtained, we have no conclusive evidence as yet that it is the dehydrated form. Sulphuric acid was found to dissolve both the yellow addition product (I) and the crimson-red product (2), with the formation of a pink aqueous solution. The addition of an excess of alkali changed

I. Jour. Am. Chem. Soc. 31, 1053.

fresh-colored reaction product is the hydrochloride of the yellow addition product (I) which gradually breaks up with the formation of aminoazobenzene hydrochloride,



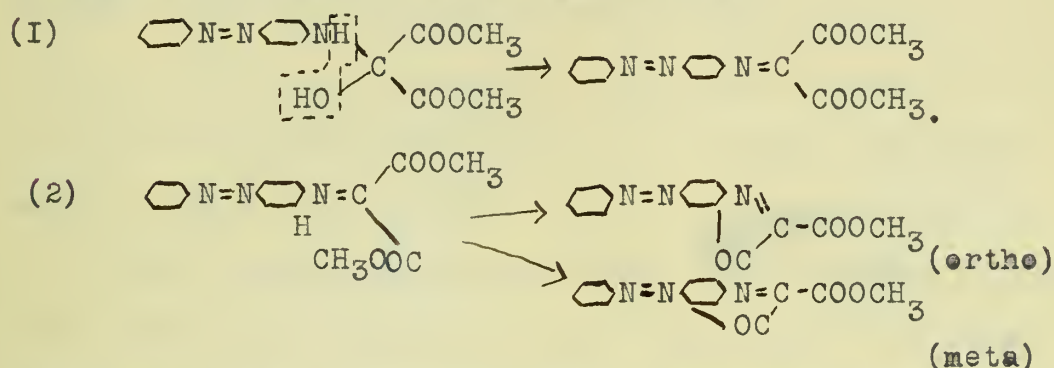
On the other hand, there is the possibility that it is the labile tautomeric form of aminoazobenzene hydrochloride which has been separated out by Vorländer^I, Thiele², and Hantzsch and Hilscher³ in their work on aminoazobenzenes and their two series of tautomeric colored salts. A molecular rearrangement and the formation of a quinoid structure takes place:



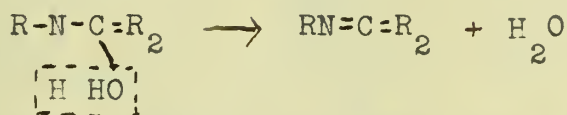
Attempts were made to reduce the azo group, -N=N-, in the yellow addition product (I) in order to obtain a leuco reaction product, but without success. The reduction of the azo group requires a strong reducing agent like tin and hydrochloric acid, and the use of this would undoubtedly result in the saponification of the ester.

1. Ber. 36, 1486.
2. Ibid. 36, 3985.
3. Ibid. 41, 1171.

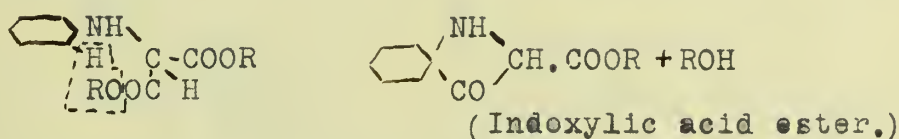
When the yellow addition product (I) is heated a slightly darker yellow, and exceedingly stable substance results. It is possible that this new substance is a dehydration or a dealcoholation product, or a combination of both as shown by the following formulae:



The primary addition product of an amine upon a keto group, in the case of methyl oxomalonate^I, has been found to lose water readily, and give the N=C group which is typical of the usual final reaction product of a substituted amine upon ketone and aldehyde groups:



In a similar manner Blank² found that when anilinomalonic acid ester was heated, alcohol was eliminated with the formation of an indoxyl ring, according to the following:



I. Curtiss and Spencer, Jour. AM. Chem. Soc. 31, 1057.

2. Ber., 31, 1814.

EXPERIMENTAL.

Bk.I.,
P92 &
IOO.

Action of Aminoazobenzene on Methyl Oxomalonate.

The aminoazobenzene was purified by recrystallization from ligroin and melted at 126 degrees. The methyl oxomalonate was prepared according to the method of Curtiss and Spencer^I and kept in the weighed container into which it had been distilled. Throughout the entire experiment great care was taken not to expose the ketone ester to the action of the air.

1.35 grams of aminoazobenzene were dissolved in the least amount of sodium-dry ether (4.2 c.cm.) and then slowly added to 1 gram of methyl oxomalonate (molecular quantities) without the exposure of the latter to the air. A reaction took place immediately with the evolution of considerable heat, the temperature rising quite rapidly from 27 degrees to 40 degrees. It then dropped to 37 degrees and a yellow brown mass crystallized out. This reaction mass is best purified by two crystallizations from sodium-dry ether. The canary yellow product melts at 135 degrees, forming a cherry red liquid. If an excess of ether is not used in dissolving the aminoazobenzene, the heat of the reaction evaporates off all of the ether, and leaves the reaction product almost completely dry.

The substance was dried in a vacuum over concentrated sulphuric acid, and analysed;

.....
I. Jour. Am. Chem. Soc. 31, 1054.

Bk.I, I - 0.20415 grams of substance gave 22.5 c.c. N at 24
P 118. degrees and 735.32 mm.

II - 0.18215 grams of substance gave 20.5 c.c. N at 24
degrees and 732.3 mm.

III - 0.2159 grams of substance gave .4741 grams CO₂ and
.1006 grams H₂O

IV - 0.1799 grams of substance gave .3928 grams of CO₂
and .0836 grams H₂O.

Theory for $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4\text{NH}-\text{C}(\text{HO})(\text{COOCH}_3)_2$,

C, 59.47 ; H, 4.95; N, 12.24;

Found, :

C, 60.06; 59.53; H, 5.17; 5.15; N, 12.25; 12.39.

The substance is methyl phenylazophenylaminotar-
tronate, and represents the primary addition product in
the reaction of an amine on a ketone or aldehyde group.

Bk.I,
P 128.

It is very soluble in acetone; easily soluble in
acetic ether and chloroform; fairly soluble in sodium-
dry ether, absolute ethyl and methyl alcohol, and ben-
zene; slightly soluble in toluene, carbon bisulphide,
and carbon tetrachloride; very slightly soluble in ligroin,
and insoluble in water.

Concentrated sulphuric acid dissolves it with the
formation of a blood red solution which becomes pink on
dilution. The addition of an excess of alkali changes
the color to sulphur yellow. If acid is again added, the
pink color returns There is here, evidently, a substance

which displays the characteristics of an indicator.

Bk II, Attempts to Reduce Methyl Phenylazophenylaminotarttronate.
P 42.

The reduction of methyl phenylazophenylaminotarttronate should eliminate the azo group, and produce a colorless reaction product. The azo group requires a strong reducing agent. Generally, tin and concentrated hydrochloric acid or zinc and sodium hydroxide are used with the application of considerable heat. In the reduction of the above substance, however, hot acid or alkaline reducing agents would cause saponification and yield poor results.

A series of test tube experiments was tried. Some of the yellow addition product was dissolved in absolute alcohol, and small chips of metallic sodium were added, the temperature being kept down by means of an ice bath. There was no change in the color of the solution; it remained yellow. Sodium alcoholate was formed.

A little zinc dust was added to a test tube containing dilute hydrochloric acid and warmed. To this solution was added a little of the substance, and heat was gently applied. The substance dissolved leaving a pink solution. The above experiment was then repeated using a 30% solution of acetic acid in place of the dilute hydrochloric. As before, a pink solution resulted.

Finally, some of the yellow product was put into a small glass stoppered bottle, a little distilled water added, and then tin and concentrated hydrochloric acid. Heat

was applied . The yellow substance turned red, and then gradually dissolved leaving a colorless solution. Loss of color indicates reduction either after or before the dissociation into the amine.

Bk II, Action of Phosphorous Pentoxide on Methyl Phenylazo-
P 18 & phenylaminotartrionate.
22.

A small quantity of methyl phenylazophenylamino-tartrionate was dissolved in sodium-dry ether, and an excess of phosphorous pentoxide was added to this solution. A solid crimson-red substance resulted almost immediately. This substance on exposure to the air rapidly turned to a blood red oil. This was probably due to the excess of phosphorous pentoxide. When added to aniline a yellow emulsion formed, and the color gradually disappeared, leaving a colorless substance which swelled and which again was probably the excess of phosphorous pentoxide. However, when some of the methyl phenylazophenylamine-tartrionate was added to a solution of phosphoric acid, the same crimson-red product was obtained. This fact leads us to doubt that this product is the dehydrated form that we expected to obtain.

As in the case of the yellow addition product(I), concentrated sulphuric acid dissolves this crimson-red substance with the formation of a pink solution when diluted. The addition of an excess of alkali changes the color to green. Here again there is evidence of an indicator.

Bk. II,
P 46. Action of Hydrochloric Acid Gas on Methyl Phenylazo-phenylaminotartrionate.

Dry hydrochloric acid gas was passed into a sodium-dry ether solution of methyl phenylazophenylaminotartrionate. The ethereal solution was bright yellow. Almost immediately a flesh-colored precipitate was formed. As the passage of the gas was continued, this precipitate gradually became darker, and finally assumed a very dark blue color. The ethereal solution had changed from a bright yellow to red. The flesh-colored product first formed in the reaction gradually changed to the darker substance on exposure to the air. When the dark blue reaction product was successively warmed with twice its weight of alcohol, then concentrated ammonia added till it dissolved, and finally water added, a yellow precipitate was produced. This was found to be aminoazobenzene melting at 126 degrees. Hydrochloric acid gas decomposes methyl phenylazophenylaminotartrionate, with the formation of the hydrochloride of aminoazobenzene. The yellow product first formed might be the hydrochloride of the undissociated yellow phenylazophenylaminotartrionate or the leuco salt of the aminoazobenzene hydrochloride.

Bk II,
P 58 Action of Hydrogen Sulphide on Methyl Phenylazophenylaminotartrionate.

Hydrogen sulphide dried over calcium chloride was passed into a sodium-dry ether solution of methyl phenylazophenylaminotartrionate. The bright yellow

ethereal solution immediately and gradually changed to a cherry red. After 20-30 minutes a purplish red crystalline precipitate formed which melted at 205 degrees, after being washed with ether and dried. It was not studied further.

Bk. II,
P 66 Effect of Heat on Action of Aminoazobenzene and Methyl Oxomalonate.

1.35 grams of aminoazobenzene, dissolved in sodium-dry ether, were added to one gram of methyl oxomalonate according to the method already described (page 8). At this point, the reaction product thus obtained was heated on a paraffin bath, in a flask, bearing a thermometer and delivery tube, for 15 minutes until it had reached a temperature of 120 degrees, and then, was held at this temperature for thirty minutes longer. The contents of the flask turned to a blood red gum. This gum was recrystallized twice from sodium-dry ether, yielding a yellow product, which melted at 158 degrees, forming a red liquid.

It seemed to be an exceedingly stable substance. It boiled in a test tube without any apparent decomposition, forming a red liquid which condensed easily on the sides of the tube and flowed back. Even when boiled with a strong solution of caustic soda, it did not decompose. When fused in a test tube with the solid sodium hydroxide, it was slowly decomposed with the formation of a light yellow, fluffy deposit on the cooler parts of

the tube. This yellow deposit looked as if it might be a sublimation product. On the application of heat it melted to a sort of light red oil, and passed up higher on the tube. If, when fusing the substance, a small amount of water was added, the yellow sublimation decomposition product passed off in the steam as yellow vapors. The original product, before fusion with caustic soda, did not distil with steam.

Bk.II, P 74 The analysis of the substance recrystallized twice from sodium-dry ether, and dried in a vacuum over concentrated sulphuric acid, gave the following data:

I - 0.1768 grams of substance gave 23.6 c.c. N at 26.5 degrees and 726.2 mm.

II - 0.2032 grams of substance gave 26.4 c.c. N at 25 degrees and 723.2 mm.

III - 0.1117 grams of substance gave .2734 grams CO₂ and .0589 grams H₂O.

IV - 0.1927 grams of substance gave .4701 grams CO₂ and .0977 grams H₂O.

Theory for $C_6H_5N=N \begin{array}{c} C_6H_3 \\ \diagup \quad \diagdown \\ OC \quad C-COOCH_3 \end{array} N$:

C, 65.53; H, 3.75; N, 14.33.

Found; C, 66.68, 66.52; H, 5.81, 5.60; N, 14.48, 14.12.

The percentage of nitrogen found corresponds well with the above formula. The carbon and hydrogen results obtained are high.

When a little of the methyl phenylazophenylamino-tartronate was heated in a test tube, and an oxidized copper spiral then dropped into it, the spiral was immediately reduced, as would be expected, but a distinct odor of formaldehyde was also detected. This suggests the presence of methyl alcohol, and therefore a ring formation.

Bk.II,
P 82. This new substance is very soluble in acetone; easily soluble in acetic ether and chloroform; fairly soluble in benzene, toluene, carbon bisulphide, and carbon tetrachloride. It is fairly soluble in sodium-dry ether; slightly soluble in absolute ethyl alcohol; very slightly soluble in absolute methyl alcohol; and insoluble in water. When heated with glacial acetic acid it dissolves with the formation of a red solution.

When the red gum is recrystallized from alcohol instead of ether, a yellow product of a different melting point (152 degrees) is obtained.

These new compounds will be further studied structurally.





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